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14. ABSTRACT Recent interest in room temperature ionic liquids (RTILs) was based initially on the replacement of volatile organic compounds (VOCs) used as industrial solvents with involatile liquids. RTILs also show promise for applications in fuel cells, batteries, solar cells and many other potential applications. RTILs are organic salts with low melting temperatures ($T < 100$ °C), and initially were thought to have no vapor pressure. However, some types of RTILs have been shown to distill in vacuum without decomposition. Lately, the design and choice of many ionic liquids is focused on physical properties such as miscibility, conductivity, viscosity, solubility and melting points. The details of how the chemical structure of the ionic liquid affects these various physical characteristics are not well understood. Similarly, due to the ionic nature of these liquids, their mechanism for vaporization may be dramatically different from molecular liquids, and predicting thermodynamic properties such as the heats of vaporization and heats of formation in the gas phase presents a challenge. Photoionization studies on the thermally stable 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (where the anion is also known as the bistriflamide anion) and related imidazolium bistriflamides have indicated that volatilization of these species occurs as a single ion pair. Recent ALS studies on the photoionization of other 1-alkyl-3-methylimidazolium based RTILs, show these systems can be more complex, with possible dissociative photoionization occurring at even the lowest detectable reservoir temperatures. At high temperatures, photoionization of the thermal decomposition products of the imidazolium RTILs indicates possible anion-cation reactions and possible polymerization to higher mass species. Note the increase in fragmentation in the spectra as a result of increased internal energy imparted by increased photon in energy, 10.0 eV versus 8.0 eV. These fragmentation patterns will aid in identifying the structure of the species generated in the experiment.					
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Volatilization and Thermal Decomposition Mechanisms of Room-Temperature Ionic Liquids

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Recent interest in room temperature ionic liquids (RTILs) was based initially on the replacement of volatile organic compounds (VOCs) used as industrial solvents with involatile liquids.¹⁻⁴ RTILs also show promise for applications in fuel cells,⁵⁻⁸ batteries⁹, solar cells^{10,11}, and many other potential applications. RTILs are organic salts with low melting temperatures ($T < 100$ °C), and initially were thought to have no vapor pressure. However, some types of RTILs have been shown to distill in vacuum without decomposition. Lately, the design and choice of many ionic liquids is focused on physical properties such as miscibility, conductivity, viscosity, solubility and melting points. The details of how the chemical structure of the ionic liquid affects these various physical characteristics are not well understood. Similarly, due to the ionic nature of these liquids, their mechanism for vaporization may be dramatically different from molecular liquids, and predicting thermodynamic properties such as the heats of vaporization and heats of formation in the gas phase presents a challenge.¹²⁻¹⁸ Photoionization studies on the thermally stable 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (where the anion is also known as the bistriflamide anion) and related imidazolium bistriflamides have indicated that volatilization of these species occurs as a single ion pair.¹⁹ Recent ALS studies on the photoionization of other 1-alkyl-3-methylimidazolium based RTILs, show these systems can be more complex, with possible dissociative photoionization occurring at even the lowest detectable reservoir temperatures (Figure 1a and 2a). At high temperatures, photoionization of the thermal decomposition products of the imidazolium RTILs indicates possible anion-cation reactions and possible polymerization to higher mass species (Figures 1b and 2b). Note the increase in fragmentation in the spectra in Figure 2 versus Figure 1 as a result of increased internal energy imparted by increased photon in energy in Figure 2 (10.0 eV) versus in Figure 1 (8.0 eV). These fragmentation patterns will aid in identifying the structure of the species generated in the experiment.

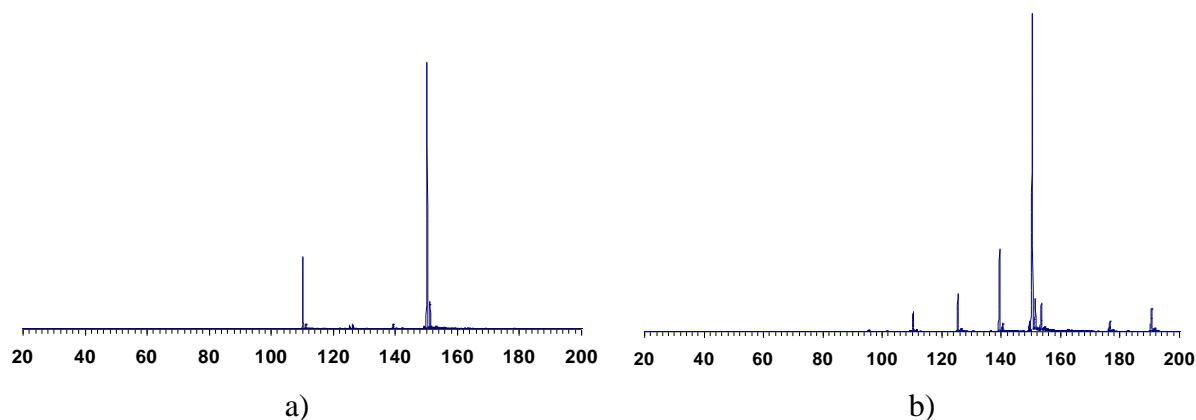


Figure 1. Photoionization mass spectrum of 1-ethyl-3-methylimidazolium dicyanamide at 8.0 eV photon energy at a) 70 °C and b) at 250 °C.

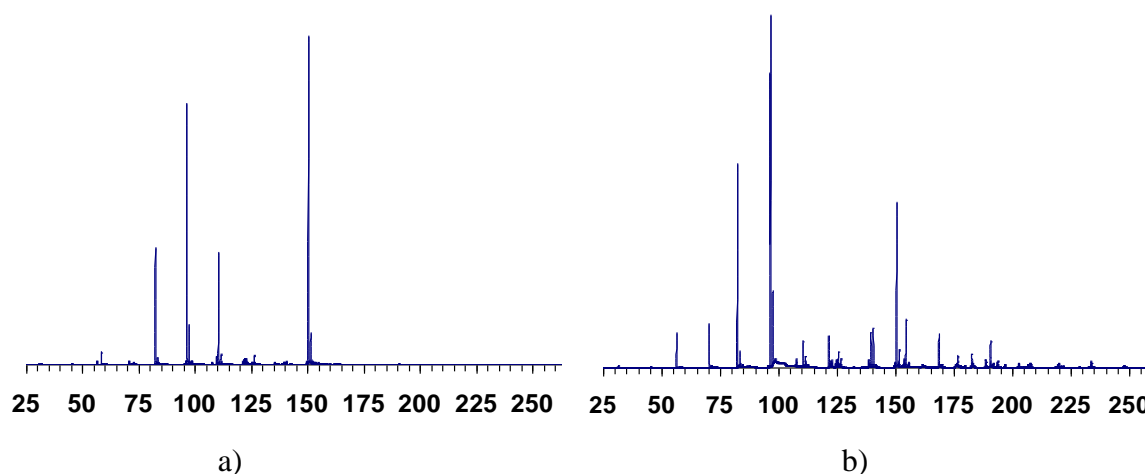


Figure 2. Photoionization mass spectrum of 1-ethyl-3-methylimidazolium dicyanamide at 10.0 eV photon energy at a) 70 °C and b) at 250 °C.

The studies of RTILs at the Advanced Light source will greatly aid in the understanding of the nature of RTILs in the gas phase, as well as begin to elucidate the thermal decomposition mechanisms of the more thermally labile RTILs. The ability to determine the appearance energies of the mass peaks allow for the identification of the products formed.

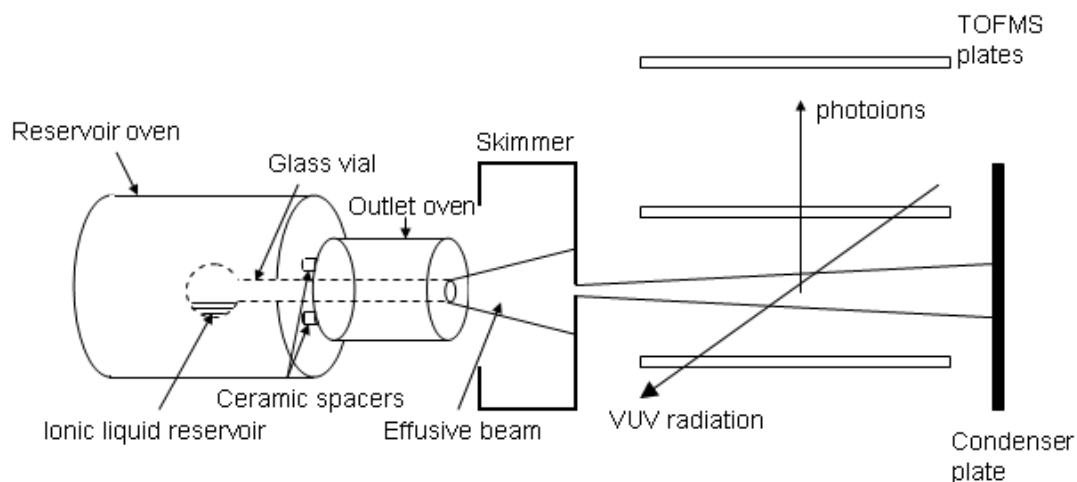


Figure 3. Schematic view of the RTIL source and interaction region for photoionization studies at the ALS.

In this work, we utilize the reflectron time of flight mass spectrometer (TOFMS) setup available at beam line 9.0.2.3 to study the photoionization of RTIL vapor. The energy resolution in this study is around 50 meV. A second generation RTIL vapor source developed in the Leone group is placed in the ionization chamber as shown schematically in Figure 3. A low density vapor is produced by heating the RTIL in a reservoir oven. This vapor effuses through a separately heated

exit tube, and it is then collimated by the aperture of the oven exit and a skimmer to produce a collimated molecular beam that will cross the ALS VUV radiation. Most of the RTIL vapor will condense on the skimmer. A dedicated collector plate is placed behind the TOFMS electrodes to condense the vapor after the interaction region. Mass spectra are taken as the oven temperature and exit tube temperatures are set between 30-350 °C and photon energies are scanned from 8.0 to 15.0 eV in 0.2 eV steps.

The purpose of having a separate oven for the RTIL reservoir and the exit tube is to be able to vaporize the ionic liquid from the reservoir at low temperature, while increasing the exit tube temperature above the decomposition temperature of the ionic liquid. This way, condensed phase reactions in the reservoir are minimized. Conversely, the exit tube temperature can be held constant and the reservoir temperature can be varied to change the effective vapor pressure of the ionic liquid. This will enable experiments which can differentiate between unimolecular and bimolecular reactions by investigating the kinetics of the products formed at different vapor pressures.

Photoionization efficiency (PIE) curves and temperature dependent mass spectra are recorded by collecting the photoions by time of flight mass spectrometry. The detection of a mass corresponding to the unfragmented parent photoion will provide unambiguous proof of the presence of isolated ion-pairs in the RTIL vapor, while the detection of higher masses will indicate larger cluster formation or polymerization reactions. Temperature dependent studies will allow the detection of RTIL thermal decomposition products. Furthermore, PIE curves will allow the determination of ionization energies of thermal decomposition products and appearance energies for their dissociative ionization products.

The initial study of 1-butyl-3-methylimidazolium dicyanamide (12/07, one 8 hour shift) indicated photoionization at low temperature, and thermal decomposition and formation of higher mass species at high temperature. More recent RTIL studies at the ALS (10/08, six 8 hour shifts) not only confirmed the initial experiment, but by systematic substitution of the cation or the anion, imply similar mechanisms to those observed in the initial study. It was also observed that RTILs can be detected in the gas phase at or near room temperature under high vacuum conditions. Data analysis of the recent experiments is currently underway.

Future work on this project will include modification of the oven source to more precisely control the temperature of the reservoir and exit tube regions. By holding the exit tube temperature constant while varying the reservoir temperature (and thus the RTIL vapor pressure), the contributions from unimolecular versus bimolecular reactions can be identified. Six shifts of beam time have been requested in the first half of 2009 to continue these experiments.

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PUBLICATIONS AND PRESENTATIONS

1. Chambreau, S. D., Vaghjiani, G. L., Strasser, D., Kostko, O., Leone, S. R., "A Study of Volatilization and Thermal Decomposition of 1-butyl-3-methylimidazolium dicyanamide by Vacuum Ultraviolet Photoionization Mass Spectrometry." Manuscript in preparation.
2. Chambreau, S. D., Vaghjiani, G. L., Strasser, D., Kostko, O., Leone, S. R., "Volatilization and Thermal Decomposition Mechanisms of Room Temperature Ionic Liquids by Vacuum Ultraviolet Photoionization." Poster presented at the Advanced Light Source Users Meeting, October 13, 2008, Berkeley, California.